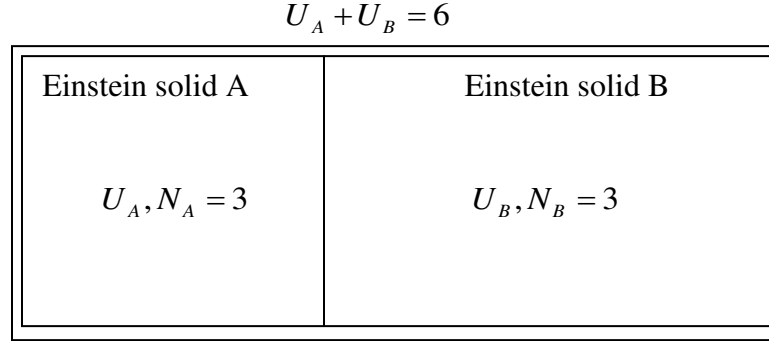


### CD221. LECTURE 3. INTERACTING EINSTEIN SOLIDS. THE POSTULATES OF THERMODYNAMICS

To gain intuition about what happens when a composite system of two Einstein solids is allowed to come into thermal contact (i.e., to exchange energy in the form of heat), let's consider a specific case in which  $N_A = N_B = 3$  and the total energy,  $U_A + U_B$  is 6 (in units of  $\hbar\omega$ .) Pictorially,



Let's also assume two other conditions: that initially, the internal constraint is adiabatic and immovable, so that both  $A$  and  $B$  are isolated from each other (and from the external surroundings), and that  $U_A = 5$  and  $U_B = 1$  (so at the outset nearly all the energy resides in  $A$ .) The initial *macrostate* of the system can therefore be characterized as  $U_A = 5$ ,  $N_A = 3$ ,  $U_B = 1$  and  $N_B = 3$ . Clearly, there will be many *microstates* that produce this macrostate. To find this number, we first find how many microstates there are for sub-system  $A$  in its initial state. The formula to use is Eq. (7) of the previous section, which gives:

$$\Omega_A = \binom{5+3-1}{5} = \binom{7}{5} = \frac{7!}{5! \times 2!} = 21 \quad (8)$$

A similar calculation for sub-system  $B$  yields

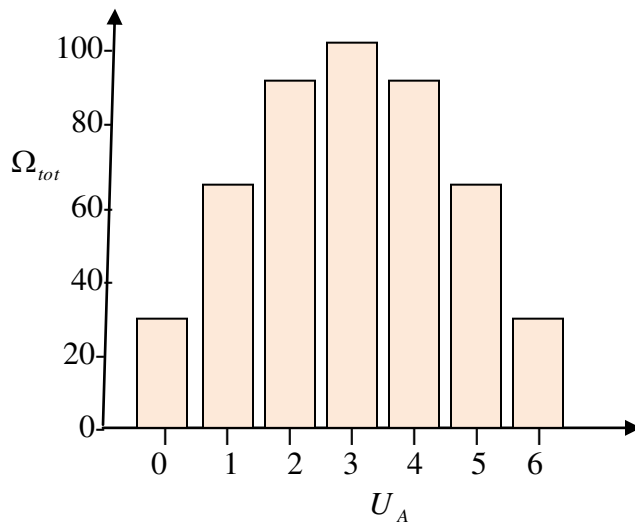
$$\Omega_B = \binom{1+3-1}{1} = \binom{3}{1} = \frac{3!}{1! \times 2!} = 3 \quad (9)$$

So for each of the 21 microstates of  $A$  that have  $U_A = 5$ , there are 3 microstates of  $B$  that have the energy  $U_B = 1$ . Which means that there are a total of 63 microstates of the composite system that have this particular division of the total energy between  $A$  and  $B$ .

In the same way, we can calculate the multiplicities of all other macrostates of the composite system that have a total energy of 6. In tabular form, the results are

Label	$U_A$	$\Omega_A$	$U_B$	$\Omega_B$	$\Omega_{total} = \Omega_A \Omega_B$
1	0	1	6	28	28
2	1	3	5	21	63
3	2	6	4	15	90
4	3	10	3	10	100
5	4	15	2	6	90
6	5	21	1	3	63
7	6	28	0	1	28

It is informative to plot these data in the form of a histogram:



Now recall that initially, prior to constraint release, the system is in the macrostate labelled 6, with  $U_A = 5$  and  $U_B = 1$ , and it is more specifically in one of the 63 possible microstates that correspond to macrostate 6 (it's not important which one.) Once the constraint is released (which in this particular example means making the initially adiabatic internal constraint diathermal), and  $A$  and  $B$  are allowed to interact through the exchange of heat (but not work), we will assume that the system settles into one or other of the microstates that are now available to the composite system as whole. (It doesn't remain forever in that state, as we've discussed, but changes from one microstate to another through the constant exchange of energy. But at some arbitrary instant of time, it would indeed be in a single well-defined microstate.)

There are 462 such microstates of the composite system, which is the number obtained by adding up all the numbers in the last column of the table. (The same number can be obtained from the formula  $\Omega(U = 6, N = 6) = \binom{6+6-1}{6}$ .) As in the case of an isolated gas, we have no means of knowing beforehand in which of these 462 microstates the system will end up at any one instant of time, so in the absence of any definite information on the matter, we'll *postulate* that the system is just as likely to be found in one particular state as it is in any other. This is essentially the procedure we had followed earlier too, in the case of the gas. But this time we'll give it a fancy name: the assumption of equal à priori probabilities, which we'll now state formally as

In a closed system in equilibrium, all accessible microstates are equally probable.

This assumption is the cornerstone of statistical mechanics, and it will be basis for all the results that we will soon derive.

In mathematical language, the assumption of equal à priori probabilities means that each particular microstate (labelled  $\alpha$ , say) occurs with probability  $1/\Omega_{tot}$ . That is,

$$p_\alpha = \frac{1}{\Omega_{tot}} = \frac{1}{462} \quad (10)$$

It's very important to note that while each of the *microstates* has the same probability of occurrence, the *macrostates* do not. For example, from our definition of probability as the ratio of favorable outcomes to total number of outcomes, the macrostate state labelled 2 has a probability given by

$$p_2 = \frac{63}{462} = 0.14 \approx 14\%$$

Similarly,

$$p_4 = \frac{100}{462} = 0.22 \approx 22\%$$

and

$$p_7 = \frac{28}{462} = 0.061 \approx 6.1\%$$

So if the system starts out in one of the microstates of the macrostate labelled 6 ( $U_A = 5, U_B = 1$ ), it will most likely end up – after constraint release – in one of the microstates of macrostate 4, where the energy happens to be equally shared between the two sub-systems.

This tendency for a system in constrained equilibrium to settle into a state where the energy is shared more or less equally after constraint release becomes more pronounced as both  $U$  and  $N$  increase. This can be illustrated with the following example:

$$N_A = 300, \quad N_B = 200, \quad U_A + U_B = 100$$

Again, let's enumerate the macrostates of this system, and their associated multiplicities. (We can anticipate that there will be 101 macrostates: ( $U_A = 0, U_B = 100$ ), ( $U_A = 1, U_B = 99$ ), ( $U_A = 2, U_B = 98$ ), ..., ( $U_A = 100, U_B = 0$ ).) As for the multiplicities, they can be calculated from the general formula  $\Omega(U, N) = \binom{U + N - 1}{U}$ ,

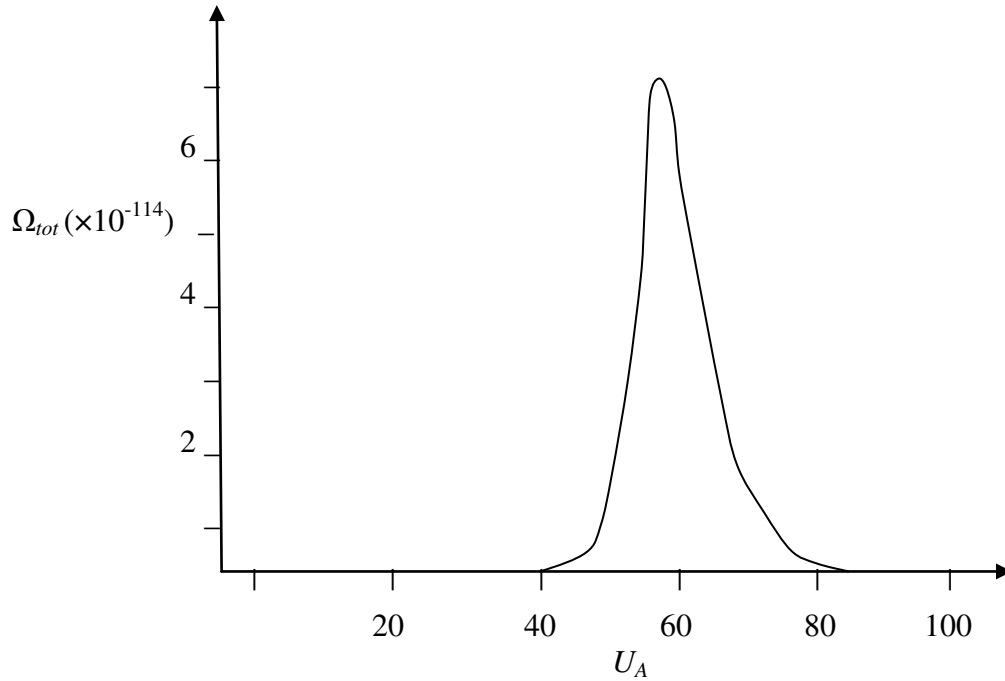
but the numbers are huge, and the calculation needs a program like Mathematica to carry out. But at the end of it, this is what we end up with (omitting some entries):

Label	$U_A$	$\Omega_A$	$U_B$	$\Omega_B$	$\Omega_{tot} = \Omega_A \Omega_B$
1	0	1	100	$2.77 \times 10^{81}$	$2.77 \times 10^{81}$
2	1	300	99	$9.27 \times 10^{80}$	$2.78 \times 10^{83}$
3	2	45150	98	$3.08 \times 10^{80}$	$1.39 \times 10^{85}$

4	3	4545100	97	$1.02 \times 10^{80}$	$4.64 \times 10^{86}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
60	59	$2.18 \times 10^{68}$	41	$3.08 \times 10^{46}$	$6.71 \times 10^{114}$
61	60	$1.30 \times 10^{69}$	40	$5.27 \times 10^{45}$	$6.85 \times 10^{114}$
62	61	$7.69 \times 10^{69}$	39	$8.82 \times 10^{44}$	$6.78 \times 10^{114}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
101	100	$1.68 \times 10^{96}$	0	1	$1.68 \times 10^{96}$

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Now the histogram of  $\Omega_A$  and  $U_A$  values would like something like this:



There are several observations we can make about the data in the above table and histogram:

In absolute terms, all of the 101 macrostates, even the ones with no energy in either  $A$  or  $B$ , have enormous multiplicities, i.e., a huge number of microstates associated with them. But more significant is the fact that the ratio of these multiplicities can be large. For instance, there are about  $10^{33}$  times as many microstates with  $U_A$  around 60 (and  $U_B$  around 40) as there are microstates with  $U_A$  around 0 (and  $U_B$  around 100.) These numbers become more striking when you translate them into probabilities.

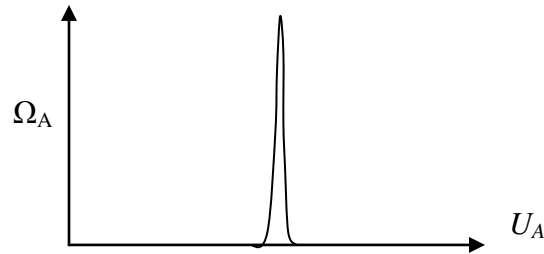
There are a total of  $9 \times 10^{115}$  microstates. This is the number you get when you add up the numbers in the right hand column of the above table. The probability that the system is found in, say, the macrostate with  $U_A = 60$  is the ratio of the number of microstates with this energy to the total number of microstates. That is,

$$\frac{6.9 \times 10^{114}}{9 \times 10^{115}} \approx 0.07 = 7\%$$

This is not particularly large (even though the  $U_A = 60$  macrostate is the most probable of all such states), and there are quite a few microstates in the vicinity of  $U_A = 60$  (both slightly above and slightly below it) that are almost as equally probable. But as you move further and further away from this macrostate, the corresponding probabilities drop precipitously, so much so that the probability that  $U_A < 30$  or  $U_A > 90$  is (literally) less than 1 in a million, and the probability that  $U_A < 10$  is less than  $10^{-20}$ . To put that last number in perspective, recall that the age of the Universe is only on the order of  $10^{18}$  seconds, which means that even if you could run through states at the rate of 100 every second, you'd still have to wait on the order of the age of the Universe before you could reasonably expect to see the system with  $U_A < 10$ . As for seeing it in the macrostate with all the energy exclusively in  $A$  or  $B$ , the chances of that happening are virtually nil.

But you could, of course, by some means arrange things so that initially all of the 100 units of energy of the system was indeed concentrated in, say,  $B$  alone. If you then allowed  $B$  to interact thermally with  $A$  by removing the adiabatic internal constraint that initially separated them, there would be a sharing of the energy, and the system would eventually settle into a new equilibrium condition in which the most probable macrostates were the ones that were the most populated. In these macrostates, the energy tends to be distributed 60:40 between  $A$  and  $B$ . In other words, from a highly non-uniform (or ordered) condition at the beginning (all the energy in  $B$ ), the system evolves to a condition of maximum uniformity (or greatest disorder) at the end.

As large as it may seem to be, a closed composite system of 500 particles and 100 units of energy is still far from being of truly macroscopic dimensions. You really need to be dealing with particle numbers on the order of  $10^{23}$  to get into that regime. And when you do that, the effects described above become still more pronounced. For instance, the histogram of total multiplicity versus subsystem energy would now look something like this:



For this system, it is now even more overwhelmingly likely that if it started out with all or most of its energy in  $A$  or  $B$ , it would, after the removal of the adiabatic constraint separating them, share this energy more or less equally between the two. Again, the direction of evolution of the system is from a condition of high non-uniformity (or great order) to one of high uniformity (or great disorder.) We could even conclude that as a general rule:

### **Systems evolve to maximize multiplicity**

We'll have to try and translate this rule, which we've derived from the study of highly idealized systems, into a set of very general principles that we'll hope are applicable to any kind of macroscopic piece of matter. Following Callen, we'll enunciate these principles as a series of *postulates*. We'll accept the validity of these postulates provisionally, and then use them to make predictions about the behavior of matter that we'll then test against the facts of experience. If the two are consistent, we'll have reasons to believe that our postulates are correct.

Sec. 1-10 of Callen provides some of the preliminary details of this postulatory approach to the study of thermodynamic problems.

But before postulating anything, let's summarize the key takeaways from our discussions of the dilute non-interacting gas and the interacting Einstein solid. These are:

- (1) Matter in bulk is made up of atoms in ceaseless motion.
- (2) A closed (i.e., isolated) system made up of some number of particles (say,  $N$ ) can be characterized completely at a macroscopic level by specifying the values of just a few gross properties. When this is done, the system is said to exist in a definite *macrostate*. The properties that define the macrostate remain unchanged over time, but their values can exhibit instantaneous small deviations. A system in such a macrostate is said to be in equilibrium. The system can also be characterized at a microscopic level by specifying the values of some property of every one of the system's constituent particles. When this is done, the system is said to exist in a definite *microstate*.

(3) For every macrostate of the system, there are in general many microstates that correspond to it. The number of such microstates is called the *multiplicity* or *degeneracy* of the macrostate.

(4) The process of change in natural phenomena can be thought of as an instance of what happens when the internal constraint in a closed composite system is removed, and all of thermodynamics can be said to be concerned with finding the solution to one all-encompassing problem, which is

**To determine the equilibrium state that results from the removal of internal constraints from a closed composite system.**

(5) Systems change their states when internal constraints are removed because of a tendency to produce as uniform, or disordered, a final state as possible. Systems change, in other words, to *maximize multiplicity*.

We'll now regard these conclusions as reflective of deeper principles that are true of any thermodynamic system, no matter how complicated, and not just of the idealized systems we've been talking about so far. These principles are embodied in the following postulates (of which there are four):

**Postulate I. The equilibrium state of a *simple* system (one that is homogeneous, isotropic, uncharged, has no surface effects, and is not subject to external fields) is completely characterized by the energy  $U$ , the volume  $V$  and the number of moles  $N$  (or equivalently, the number of particles.)**

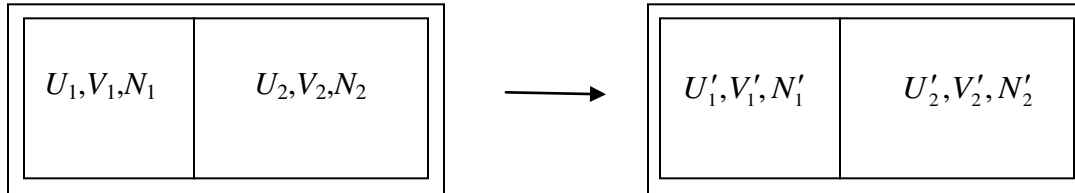
We've already seen that the energy and the number of particles (or the amount of matter) are properties that are descriptive of the system as a whole, and have the requisite quality of being essentially time-independent, which is necessary when talking about the state of equilibrium. The reason for including the volume  $V$  of the container that encloses a system as another parameter that is generally required to characterize the system's macrostate fully is the following: We've seen that in a state of equilibrium, the particles that make up a system have achieved their maximal degree of uniformity, both in respect of their spatial distribution in the container as well as in the way energy is shared or spread out among them. Knowing  $V$ , then, we can immediately deduce how many molecules  $N_s$  there are in any sub-volume  $V_s$  of the container; that number is given by  $N_s = N(V_s/V)$ . In the same way, we can deduce the average energy per particle of the molecules in that sub-volume, which is  $U/N_s$ . So these 3 parameters tell us pretty much whatever we want to know about the system at the macroscopic level.

But there are actually much better reasons for why  $U$ ,  $V$  and  $N$  are postulated to describe the macroscopic state of the system completely. These reasons are related to a mathematical relation known as Noether's theorem, which basically tells you from first principles which gross features of a system are time-independent and therefore qualify as thermodynamic variables. A discussion of Noether's theorem and what it means for thermodynamics can be found in Sec. 21-3. There you'll also find out why, if it's



assumed that only  $U$ ,  $V$  and  $N$  are necessary to describe a macrostate, it's necessary also to restrict our attention to systems that are homogeneous, isotropic, uncharged, have no surface effects, and are not subject to external fields.

In the context of Postulate I, we see that the fundamental problem of thermodynamics can be described by the following figure:



which reduces the problem to that of finding  $U'_1, V'_1, N'_1$  and  $U'_2, V'_2, N'_2$  given  $U_1, V_1, N_1$  and  $U_2, V_2, N_2$ .

- The driving force behind the tendency to change

From our study of the *microscopic* behavior of simple systems, we have a sense now of why the transformation illustrated above might take place; it is because after constraint release the composite system on the left is driven to populate those macrostates that have the greatest multiplicity. These macrostates are maximally uniform in some sense (either in the way energy is more or less equally shared among all the particles, or in the way these particles are more or less equally spread out over the space available to them.) We've seen that this tendency towards greater uniformity when the system and its surroundings come into contact is manifested in the maximization of a microscopic property, viz., the multiplicity. An obvious question is the following: Is there some measurable *macroscopic* property of the system that is similarly maximized after a change of state? At the moment, we know of no such property, but we'll nevertheless assume, based on what we do know about what happens at the microscopic level, that one does in fact exist. We'll express assumption in the form of a second postulate:

**Postulate II. For every equilibrium state of a simple system there exists a function called the entropy,  $S$ , that depends on  $U$ ,  $V$  and  $N$ . In the absence of an internal constraint, the final equilibrium state of a closed composite system is one where  $U$ ,  $V$  and  $N$  assume values that maximize  $S$  over the manifold of constrained equilibrium states.**

To understand what this postulate means, consider, by way an example, a composite system of energy  $U$  (at fixed and unchanging values of  $V$  and  $N$ ) whose sub-systems have energies  $U_A^{(1)}$  and  $U_B^{(1)}$  such that  $U_A^{(1)} + U_B^{(1)} = U$ . By postulate II, this composite system has a definite entropy, say,  $S_1$ . Suppose there exists another composite system of the

same total energy  $U$  that is identical to the first except that  $A$  and  $B$  have the energies  $U_A^{(2)}$  and  $U_B^{(2)}$ , such that  $U_A^{(2)} + U_B^{(2)} = U$ . By postulate II, this composite system also has a definite entropy, say  $S_2$ , which in general is different from  $S_1$ . A whole set (or manifold) of such composite systems can be imagined that differ only in how much of  $U$  is partitioned between  $A$  and  $B$ . Each member of this set has a definite entropy, but by postulate II, in only one (call it system  $M$ ) is this entropy the largest. Postulate II goes on to assert that if the internal constraint in any of the systems in this manifold were made diathermal, allowing energy exchange between  $A$  and  $B$ , it would evolve to system  $M$ , and the energies of  $A$  and  $B$  would assume the values that characterized  $M$ .

Since we've argued that the behaviour of  $S$  mirrors, at the macroscopic level, the behavior of  $\Omega$ , we expect that the two are connected in some way. In other words,

$$S \sim \Omega$$

To make this connection more precise, we'll need to see if there are other properties of the entropy that we can reasonably infer or postulate.

- Other properties of the entropy

The interpretation we've given to the entropy – as something that measures the tendency for systems to become maximally uniform – allows us to intuit some other properties.

Consider, for instance, a system with fixed  $V$  and  $N$ , and imagine that it gains some energy. Because there is now more energy available for distribution, it seems reasonable to suppose that the entropy likewise increases. It likewise seems reasonable to suppose that entropies, like  $U$ ,  $V$  and  $N$ , are additive, meaning, more specifically, that the entropy of a composite system is the sum of the entropies of the sub-systems. And finally, because thermodynamics is concerned with large systems, we expect that any changes that might be made to  $U$ ,  $V$  and  $N$  in such systems would not produce abrupt or drastic changes in  $S$ .

All these considerations suggest that we can assert the following:

**Postulate III. The entropy of a composite system is additive over its constituent sub-systems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.**

Does this further postulate allow us to determine the relation between  $S$  and  $\Omega$ ? In fact it does, for the following reason: When two systems with initial multiplicities  $\Omega_A$  and  $\Omega_B$  come together, the multiplicity of the combined system is the *product* of these two numbers. Multiplicities, in other words, as their name suggests, are multiplicative in nature. But the entropy, as we've just postulated, is additive. The only way to relate  $S$  and

$\Omega$  to each other, and at the same time preserve their additive and multiplicative character is if this relation is of the form

$$S \sim \ln \Omega$$

This way, if  $\Omega = \Omega_A \Omega_B$ , it would follow that  $S \sim \ln \Omega_A + \ln \Omega_B = S_A + S_B$ . We'll assume then that the connection between  $S$  and  $\Omega$  is indeed of the above form. It only remains now to convert this relation into an equality, and we'll do this by introducing a proportionality constant. So finally,

$$S = k_B \ln \Omega$$

where we refer to  $k_B$  as Boltzmann's constant. We'll have more to say about this later. For the moment, it's enough to note that the above equation, also called the Boltzmann equation, is the central relation of statistical thermodynamics. It connects a microscopic property of the system (that hopefully we can somehow determine) to a macroscopic property that governs bulk behavior.

Before discussing examples of the application of the Boltzmann equation to real systems (or at least to idealized representations of real systems), let's continue exploring some of the other consequences of our postulates.